

**Synthesis and Crystal Structures of (Fulvalene)W<sub>2</sub>(SH)<sub>2</sub>(CO)<sub>6</sub>,  
(Fulvalene)W<sub>2</sub>(μ-S<sub>2</sub>)(CO)<sub>6</sub>, and (Fulvalene)W<sub>2</sub>(μ-S)(CO)<sub>6</sub>—Low Valent  
Tungsten Carbonyl Sulfide and Disulfide Complexes Stabilized by the  
Bridging Fulvalene Ligand**

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Vollhardt,<sup>§,\*</sup> and Carl D. Hoff<sup>†,\*</sup>**

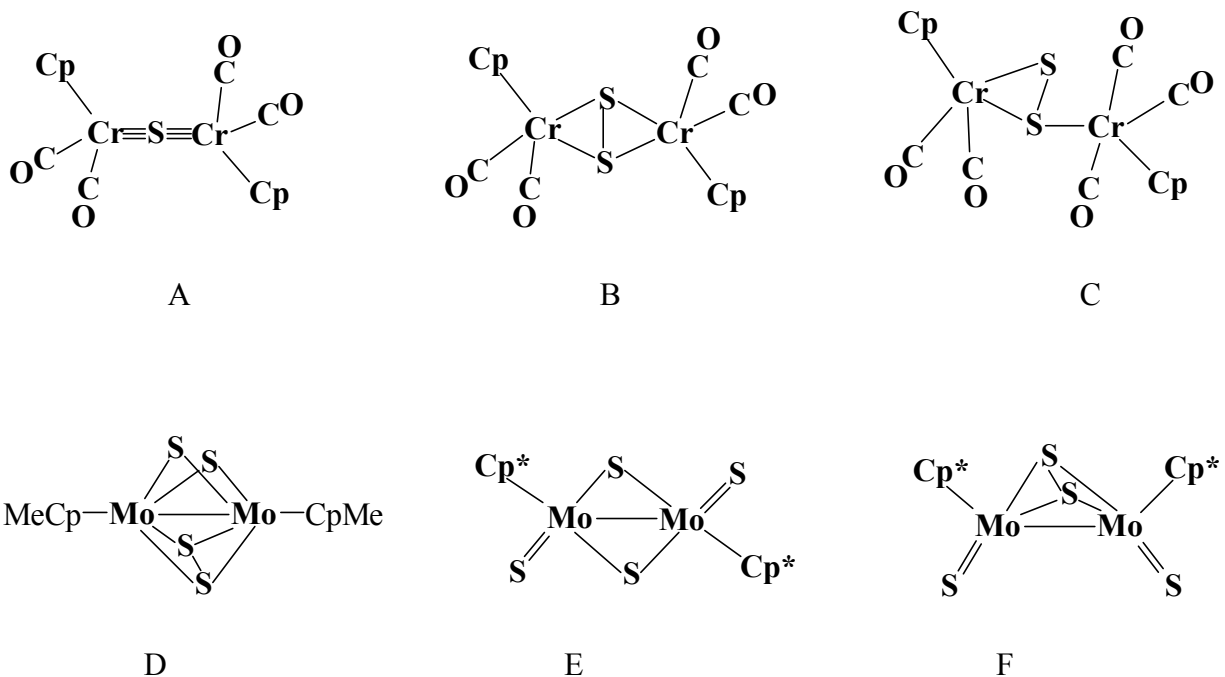
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## Abstract

Reaction of  $\text{FvW}_2(\text{H})_2(\text{CO})_6$  with  $2/8 \text{ S}_8$  in THF results in rapid and quantitative formation of  $\text{FvW}_2(\text{SH})_2(\text{CO})_6$ . The crystal structure of this complex is reported and shows that the two tungsten-hydrosulfide groups are on opposite faces of the fulvalene ligand in an anti configuration. Nevertheless, treatment of  $\text{FvW}_2(\text{SH})_2(\text{CO})_6$  with  $\text{PhN=NPh}$  produces  $\text{FvW}_2(\mu\text{-S}_2)(\text{CO})_6$  and  $\text{Ph(H)N-N(H)Ph}$ . The crystal structure of the bridging disulfide, which cocrystallizes with  $\text{FvW}_2(\text{SH})_2(\text{CO})_6$  in a 2:1 ratio, is also described. Exposure of  $2 \text{ •Cr(CO)}_3\text{C}_5\text{Me}_5$  to  $\text{FvW}_2(\text{SH})_2(\text{CO})_6$  effects similar H atom transfers yielding  $2 \text{ HCr(CO)}_3\text{C}_5\text{Me}_5$  and  $\text{FvW}_2(\mu\text{-S}_2)(\text{CO})_6$ . Attempts to obtain crystals of the latter from solutions derived from this reaction mixture furnished a third product,  $\text{FvW}_2(\mu\text{-S})(\text{CO})_6$ , which was analyzed crystallographically. The enthalpy of sulfur atom insertion into  $\text{FvW}_2(\text{H})_2(\text{CO})_6$  yielding  $\text{FvW}_2(\text{SH})_2(\text{CO})_6$  has been measured by solution calorimetry.

## Introduction

The goal of this work was to begin the investigation of the basic sulfur chemistry of fulvalene bridged group metal-metal complexes of group VI. The reactions of analogous cyclopentadienyl systems has yielded a number of interesting dimeric structural types as shown in Scheme 1:

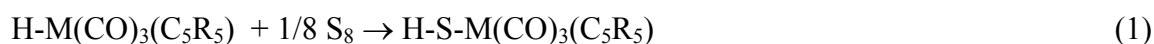


Cyclopentadienyl chromium carbonyl complexes with one or two bridging sulfur atoms (A-C) have been prepared by the groups of Legzdins,<sup>1</sup> Goh,<sup>2</sup> and Herrmann,<sup>3</sup> whereas cyclopentadienyl molybdenum sulfido complexes of the type D-F have been investigated by the groups of Rakowski Dubois<sup>4</sup> and Wachter.<sup>5</sup> The crystal structure of  $\text{Cp}(\text{CO})_3\text{W-S-W}(\text{CO})_3\text{Cp}$  has been reported,<sup>6</sup> as well as that of the mixed valence complex  $\text{Cp}_2\text{W}_2(\text{CO})_2(\text{S}_2)$ .<sup>5</sup>

There are no published structures of fulvalene (Fv) complexes analogous to those shown in Scheme 1 for the more familiar cyclopentadienyl systems of the group VI metals. Such compounds could conceivably display quite distinct scaffolds and reactivities due to additional

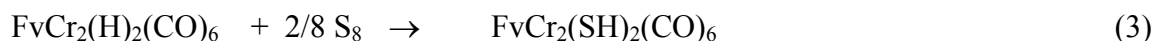
constraints imposed on metal stereochemistry by the bridging fulvalene ligand. In fact, to the authors' knowledge, the only structural data on a fulvalene bridged sulfido complex are for the Zr(IV) dimer (Fv)(CpZrS)<sub>2</sub>.<sup>7</sup>

Recently we described the structural and calorimetric study of sulfur atom insertion<sup>8</sup> into group VI metal hydrides as shown in eq 1, as well as physical studies of oxidative addition<sup>9</sup> of H<sub>2</sub> to the fulvalene bridged Cr–Cr bonded dimer shown in eq 2:



This paper describes our first investigations of the chemistry of fulvalene group VI metal sulfur containing complexes, including synthetic, structural, and calorimetric studies of the complexes FvW<sub>2</sub>(SH)<sub>2</sub>(CO)<sub>6</sub>, FvW<sub>2</sub>(μ-S<sub>2</sub>)(CO)<sub>6</sub>, and FvW<sub>2</sub>(μ-S)(CO)<sub>6</sub>.

During the course of this work, Shaver and Kovács<sup>10</sup> reported the synthesis of FvW<sub>2</sub>(SH)<sub>2</sub>(CO)<sub>6</sub>, as shown in reaction 3, and other examples of the sulfur chemistry of Fv dimetals are scarce.<sup>11</sup>



## Experimental Section

**General Procedures.** All manipulations were carried out under an argon atmosphere using standard Schlenk tube and glove box techniques. Toluene, THF, and C<sub>6</sub>D<sub>6</sub> were distilled from Na/benzophenone prior to use. Methylene chloride was distilled from P<sub>2</sub>O<sub>5</sub>. Analytical reagent grade heptane was degassed prior to use. The complexes FvW<sub>2</sub>(CO)<sub>6</sub> and

$\text{FvW}_2(\text{H})_2(\text{CO})_6$  were prepared as described in the literature.<sup>12</sup> FTIR data were obtained on a Perkin Elmer System 2000, NMR spectra on a Varian VXR-400 spectrometer. Calorimetric measurements were performed using a Setaram C-80 calorimeter. Crystal structures were determined using Siemens SMART diffractometers at either the University of California [for  $\text{FvW}_2(\mu\text{S}_2)(\text{CO})_6$ ] or the University of Florida [for  $\text{FvW}_2(\mu\text{S})(\text{CO})_6$  and  $\text{FvW}_2(\text{SH})_2(\text{CO})_6$ ].

**Preparation of  $\text{FvW}_2(\text{SH})_2(\text{CO})_6$  and Crystal Growth.** A solution of 0.0527 g  $\text{S}_8$  in approximately 4 mL of THF was added to a solution of 0.503 g of  $\text{FvH}_2\text{W}_2(\text{CO})_6$  in approximately 15 mL THF at 0 °C. Upon mixing the reagents, the Schlenk tube was immediately evacuated while still in the ice bath and the volume reduced to 7-8 mL over a 5-10 min period. Spectroscopic monitoring of the reaction by FTIR showed it to be complete in less than 1 min. To this solution was added 20 mL of degassed heptane. Storing at 0 °C resulted in precipitation of an orange crystalline solid that was spectroscopically pure (0.383g, 69%). IR spectra revealed bands at 2026 and 1939  $\text{cm}^{-1}$  in toluene and 2024 and 1935  $\text{cm}^{-1}$  in THF, whereas  $^1\text{H}$  NMR data showed absorptions at  $\delta = 4.74, 4.33,$  and  $-2.32$  ppm in  $\text{C}_6\text{D}_6$ , as described.<sup>10</sup> The reaction was also found to occur cleanly in  $\text{CH}_2\text{Cl}_2$ . The complex  $\text{FvW}_2(\text{SH})_2(\text{CO})_6$  proved to be stable in the solid and in solution when pure and kept under inert atmosphere. Exposure to direct sunlight caused slow evolution of gas and decomposition.

**Determination of the Structure of  $\text{FvW}_2(\text{SH})_2(\text{CO})_6$ .** Single crystals suitable for structural analysis were grown by slow diffusion of heptane into a  $\text{CH}_2\text{Cl}_2$  solution of  $\text{FvW}_2(\text{SH})_2(\text{CO})_6$ . Data were collected at 173 K on a Siemens SMART PLATFORM equipped with a CCD area detector and a graphite monochromator utilizing Mo  $\text{K}_\alpha$  radiation ( $\lambda = 0.71073$  Å). Cell parameters were refined using up to 8192 reflections. A hemisphere of data (1381 frames) was collected using the  $\omega$ -scan method (0.3° frame width). The first 50 frames were

remeasured at the end of the data collection to monitor instrument and crystal stability (maximum correction on  $I$  was  $< 1\%$ ). Absorption corrections by integration were applied based on measured indexed crystal faces.

The structure was solved by the direct methods in *SHELXTL5* [Sheldrick, G. M. (1998). *SHELXTL5*. Bruker-AXS, Madison, Wisconsin, USA] and refined using full-matrix least squares. The complex has a crystallographic center of inversion located at the midpoint of the Cp-Cp bond. Thus the asymmetric unit consists of a half complex. The non-hydrogen atoms were treated anisotropically, whereas the hydrogens were calculated in idealized positions attached to their respective carbon atoms. The mercapto proton was obtained from a difference Fourier map and refined without constraints. The geometry around the W atom is a four-legged piano stool with the three CO and the HS ligands occupying the square base. A total of 123 parameters were subjected to the final cycle of refinement using 2117 reflections with  $I > 2\sigma(I)$  to yield  $R_1$  and  $wR_2$  of 2.69% and 6.49%, respectively. Refinement employed  $F^2$ .

**Reaction of  $\text{FvW}_2(\text{SH})_2(\text{CO})_6$  with  $\text{PhN=NPh}$ .** The reaction of  $\text{Fv}_2\text{W}_2(\text{SH})_2(\text{CO})_6$  with  $\text{PhN=NPh}$  was studied by FTIR spectroscopy in toluene solution ( $4.4 \times 10^{-3}\text{M}$ ) under an argon atmosphere. At RT, it required days to proceed, but at  $30^\circ\text{C}$ , over several h, a smooth decrease in the infrared bands at  $2026$  and  $1939\text{ cm}^{-1}$  due to  $\text{Fv}_2\text{W}_2(\text{SH})_2(\text{CO})_6$  was noted and a concomitant increase in bands at  $2032$ ,  $2016$ ,  $1954$ ,  $1928\text{ cm}^{-1}$ , assigned to  $\text{Fv}_2\text{W}_2(\text{S}_2)(\text{CO})_6$ . Monitoring the process by  $^1\text{H}$  NMR in  $\text{C}_6\text{D}_6$  at  $30^\circ\text{C}$  revealed the conversion of  $\text{PhN=NPh}$  to  $\text{PhNH-NHPh}$  and of  $\text{Fv}_2\text{W}_2(\text{SH})_2(\text{CO})_6$  to  $\text{FvW}_2(\text{S}_2)(\text{CO})_6$ , the latter exhibiting characteristic Fv multiplets at  $\delta = 5.7941$  and  $4.0402\text{ ppm}$ .

**Determination of the Structure of  $\text{FvW}_2(\mu\text{S}_2)(\text{CO})_6$ .** Deep purple crystals of  $\text{FvW}_2(\mu\text{S}_2)(\text{CO})_6$  (4 molecules) cocrystallizing with  $\text{FvW}_2(\text{SH})_2(\text{CO})_6$  (2 molecules) were obtained by layering the crude solution from the experiments above with heptane. Data were collected at  $173$

K on a Siemens SMART PLATFORM equipped with a CCD area detector and a graphite monochromator utilizing Mo  $K_{\alpha}$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ). Cell parameters were refined using up to 8192 reflections. A hemisphere of data (2366 frames) was collected using the  $\omega$ -scan method ( $0.3^{\circ}$  frame width). Absorption corrections by integration were applied based on measured indexed crystal faces.

The structure was solved by the direct methods in SIR92 [Altomare et al. (1993)] and refined using full-matrix least squares. To account for additional electron density in the proximity of the tungsten disulfide nuclei, a 10% W-W impurity {most likely  $[\text{FvW}_2(\text{CO})_6]$ } was included (W4, W5) in refinement and structure calculations. The measured W-W distance in the disulfide complex was  $4.99 \text{ \AA}$ . The W-W distance for the modeled tungsten impurity was  $4.00 \text{ \AA}$ , with its tungsten atoms placed  $0.67 \text{ \AA}$  and  $0.43 \text{ \AA}$  away from those in the disulfide. The positions for the hydrogen atoms were included in the final least squares calculations, but not refined. The locations of the hydrogens bonded to sulfur in the dithiol were neither included nor refined during least squares calculations. The ditungsten dithiol is oriented in the trans configuration of the fulvalene, with a W-S bond distance of  $2.504 \text{ \AA}$ . It is located on a crystallographic inversion center and the fulvalene ligand constrained to planarity. In contrast, the ditungsten disulfide complex is bonded cis with a measured dihedral angle between the cyclopentadienyl planes of the fulvalene of  $150^{\circ}$ . A total of 371 parameters were subjected to the final cycle of refinement using 2366 reflections with  $I > 3\sigma(I)$  to yield  $R_1$  and  $wR_2$  of 3.2% and 3.2%, respectively. Refinement employed  $F^2$ .

**Reaction of FvW<sub>2</sub>(SH)<sub>2</sub>(CO)<sub>6</sub> with •Cr(CO)<sub>3</sub>C<sub>5</sub>Me<sub>5</sub>.** To 15 mL of a 4.6 mM toluene solution of FvW<sub>2</sub>(SH)<sub>2</sub>(CO)<sub>6</sub> at 11°C was added 15 mL of a 9.2 mL toluene solution of •Cr(CO)<sub>3</sub>C<sub>5</sub>Me<sub>5</sub>. Reaction was complete within 1 min of mixing. IR spectral analysis indicated quantitative conversion of •Cr(CO)<sub>3</sub>C<sub>5</sub>Me<sub>5</sub> (1994, 1896 cm<sup>-1</sup>) to HCr(CO)<sub>3</sub>C<sub>5</sub>Me<sub>5</sub> (1995, 1912 cm<sup>-1</sup>) and the emergence of peaks at 2032, 2016, 1954, 1928 cm<sup>-1</sup> due to FvW<sub>2</sub>(S<sub>2</sub>)(CO)<sub>6</sub> (see above). <sup>1</sup>H NMR spectroscopy confirmed these assignments.

**Determination of the Structure of FvW<sub>2</sub>(μ-S)(CO)<sub>6</sub>.** The crude product mixture from the reaction of FvW<sub>2</sub>(SH)<sub>2</sub>(CO)<sub>6</sub> with •Cr(CO)<sub>3</sub>C<sub>5</sub>Me<sub>5</sub> (see above) was filtered into a small diameter tube and layered with heptane. Over a period of a week, orange crystals were obtained, with IR bands at 2017, 1965, 1927, and 1908 cm<sup>-1</sup> in toluene, and <sup>1</sup>H NMR peaks at δ 5.7791 and 4.7277 ppm in C<sub>6</sub>D<sub>6</sub>, spectra data quite distinct from those for FvW<sub>2</sub>(S<sub>2</sub>)(CO)<sub>6</sub> described above. Data were collected at 173 K on a Siemens SMART PLATFORM equipped with a CCD area detector and a graphite monochromator utilizing Mo K<sub>α</sub> radiation (λ = 0.71073 Å). Cell parameters were refined using up to 8192 reflections. A hemisphere of data (1381 frames) was collected using the ω-scan method (0.3° frame width). The first 50 frames were remeasured at the end of the data collection to monitor instrument and crystal stability (maximum correction on *I* was < 1%). Absorption corrections by integration were applied based on measured indexed crystal faces.

The structure was solved by the direct methods in *SHELXTL5* [Sheldrick, G. M. (1998). *SHELXTL5*. Bruker-AXS, Madison, Wisconsin, USA] and refined using full-matrix least squares. The non-hydrogen atoms were treated anisotropically, whereas the hydrogens were calculated in idealized positions attached to their respective carbon atoms. The geometry around the W atom is a four-legged piano stool with the three CO and the bridging S ligands occupying



the square base. The square planes are rotated in opposite directions along their respective normals in order to accommodate the bridging S ligand. The Cp rings are not coplanar but twisted with respect to each other with a dihedral angle of  $25.4(7)^\circ$ . A total of 227 parameters were subjected to the final cycle of refinement using 3797 reflections with  $I > 2\sigma(I)$  to yield  $R_1$  and  $wR_2$  of 2.74% and 5.69%, respectively. Refinement employed  $F^2$ .

**Calorimetric Measurements of the Enthalpy of Reaction of  $\text{FvW}_2(\text{H})_2(\text{CO})_6$  with  $2/8 \text{ S}_8$ , and of  $\text{FvW}_2(\text{SH})_2(\text{CO})_6$  with  $2 \bullet\text{Cr}(\text{CO})_3\text{C}_5\text{Me}_5$ .** In a typical procedure, a solution mixing cell of a Setaram calorimeter was taken into a glove box and loaded with 2.0 mL of a 73 mM THF solution of  $\text{FvW}_2\text{H}_2(\text{CO})_6$  and 2.0 mL of a 9.9 mM THF solution of  $\text{S}_8$ . The cell was sealed, taken from the glove box, and placed in the calorimeter. Following thermal equilibration, the reaction was initiated. After completion of the measurement (1-2 h,  $30^\circ\text{C}$ ), the cell was returned to the glove box. Analysis of the reaction mixture by FTIR spectroscopy confirmed quantitative conversion to  $\text{FvW}_2(\text{SH})_2(\text{CO})_6$ ;  $\Delta H = -9.6 \pm 0.9 \text{ kcal/mol}$ .

The calorimetry of the reaction of the  $\text{FvW}_2(\text{SH})_2(\text{CO})_6$  with  $\bullet\text{Cr}(\text{CO})_3\text{C}_5\text{Me}_5$  was measured in a similar manner. Varying, but small, amounts of  $\text{FvW}_2(\mu\text{-S})(\text{CO})_6$  and  $\text{C}_5\text{Me}_5(\text{CO})_2\text{Cr}\equiv\text{S}\equiv\text{Cr}(\text{CO})_2\text{C}_5\text{Me}_5$  were detected by IR spectroscopy in some of the runs, particularly during prolonged measurements or in the presence of excess  $\bullet\text{Cr}(\text{CO})_3\text{C}_5\text{Me}_5$ . Examination of the thermograms indicated that this side reaction did not significantly alter the measured enthalpy of the primary process, as it appeared to be nearly thermoneutral (slightly endothermic) and thus of minor consequence to the integrated heat of reaction. Nevertheless, because of its occurrence, the experimental error in this measurement is increased by 1 kcal/mol to yield  $\Delta H = -8.2 \pm 1.6 \text{ kcal/mol}$ .

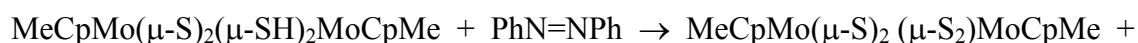
**Attempted Reaction of FvW<sub>2</sub>(S<sub>2</sub>)(CO)<sub>6</sub> with H<sub>2</sub>.** In a glove box, 20 mL of an approximately 4 mM toluene solution of FvW<sub>2</sub>(S<sub>2</sub>)(CO)<sub>6</sub> was filtered into a high pressure FTIR cell (Harrick Scientific) and fitted with a 40 mL Hoke bomb autoclave and quartz pressure transducer (Omega Scientific). The apparatus was removed from the glove box and taken to a manifold where it was filled with 1000 psi pressure of research grade (99.995 %) H<sub>2</sub> (Matheson Gas). There was no measurable change over a period of 2d at RT. After one month, some FvW<sub>2</sub>(μ-S)(CO)<sub>6</sub> was detected, but no FvW<sub>2</sub>(SH)<sub>2</sub>(CO)<sub>6</sub>.

## Results and Discussion

The fulvalene bridge between two transition metals constitutes a scaffold that is continuing to give rise to unusual dinuclear complex chemistry.<sup>9-13</sup> It is therefore surprising that sulfur as an element has played a very limited role in these investigations,<sup>7,10,11</sup> despite its extensive role as a ligand in complexes ranging in relevance from (potential) catalysts, new materials, and biomimetics, to models for surfaces.<sup>14</sup> This study marks the beginning of a program aiming to remedy this situation and deals with the FvW<sub>2</sub> nucleus as a representative of the group VI FvM<sub>2</sub> complexes. Our results have to be viewed within the context of the chemistry of the related (CpM)<sub>2</sub> systems depicted in Scheme 1. In particular, complex D has



been shown to activate H<sub>2</sub> as in eq 4,<sup>4a</sup> and the resulting hydrosulfide to be capable of reducing azobenzene as in eq 5.<sup>4a,b</sup> Reactions (4) and (5) provide a route for the catalytic hydrogenation

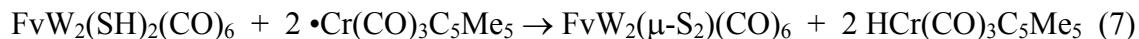
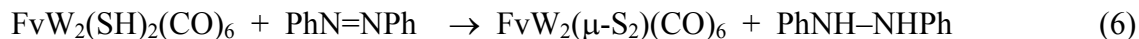


of azobenzene.<sup>4</sup> In addition, the catalytic reduction of SO<sub>2</sub> by Cp\*Mo(μ-S)<sub>2</sub>(μ-S<sub>2</sub>)MoCp\* was discovered by Kubas and coworkers.<sup>15</sup>

**Preparation of FvW<sub>2</sub>(SH)<sub>2</sub>(CO)<sub>6</sub>, FvW<sub>2</sub>(μ-S<sub>2</sub>)(CO)<sub>6</sub>, and FvW<sub>2</sub>(μ-S)(CO)<sub>6</sub>.** Reaction of the FvW<sub>2</sub>(H)<sub>2</sub>(CO)<sub>6</sub> with two equivalents of S<sub>8</sub> producing FvW<sub>2</sub>(SH)<sub>2</sub>(CO)<sub>6</sub> as shown in eq 3 and reported by Kovacs and Shaver<sup>10</sup> in acetone was found by us to proceed rapidly in THF or CH<sub>2</sub>Cl<sub>2</sub> in quantitative yield. Spectroscopic data reported here are in essential agreement with the literature data. In contrast to the reported instability of FvW<sub>2</sub>(SH)<sub>2</sub>(CO)<sub>6</sub> when prepared in acetone solution,<sup>10</sup> in CH<sub>2</sub>Cl<sub>2</sub> or THF the complex appears sufficiently stable to allow the growing of X-ray quality crystals over a period of more than a week. There were no signs of decomposition provided that exposure to light was avoided. The structure of FvW<sub>2</sub>(SH)<sub>2</sub>(CO)<sub>6</sub> is shown in Figure 1.

Two reactions of FvW<sub>2</sub>(SH)<sub>2</sub>(CO)<sub>6</sub> were investigated in this report and are shown in eqs 6 and 7.

**Figure 1 here**



The reduction of azobenzene was performed in analogy to the work of Dubois<sup>4</sup> in reaction 5.

The complex FvW<sub>2</sub>(μ-S<sub>2</sub>)(CO)<sub>6</sub> was characterized by IR and NMR spectroscopic data, as well as

by X-ray crystallography as discussed below. Exposure of  $\text{FvW}_2(\text{SH})_2(\text{CO})_6$  to two equivalents of the chromium radical as shown in eq 7 also yielded  $\text{FvW}_2(\mu\text{-S}_2)(\text{CO})_6$  with spectroscopic properties identical to those observed for the tungsten sulfide from eq 6. The other reaction products [ $\text{PhNH-NHPh}$  and  $\text{HCr}(\text{CO})_3\text{C}_5\text{Me}_5$ , respectively] were identified spectroscopically to confirm the stoichiometry of the respective transformations. The rate of conversion of  $\text{FvW}_2(\text{SH})_2(\text{CO})_6$  in the presence of  $\text{PhN=NPh}$  was significantly lower than that in the presence of  $\bullet\text{Cr}(\text{CO})_3\text{C}_5\text{Me}_5$ . Thus, with both reagents in mM concentrations, reaction 6 occurred slowly over a period of hours, whereas the H atom transfer of eq 7 was complete within minutes. Additional kinetic studies of these processes are planned.

The crystals obtained from the mixtures in eqs 6 and 7 yielded different structures, despite the similarity of the spectra recorded for the crude product solutions. The crystals grown from reaction 6 were deep purple and a crystal structure determination showed them to be a cocrystallite of  $\text{FvW}_2(\text{SH})_2(\text{CO})_6$  and  $\text{FvW}_2(\mu\text{-S}_2)(\text{CO})_6$  in a 1:2 ratio. The molecular packing is shown in Figure 2 and a view of only the  $\text{FvW}_2(\mu\text{-S}_2)(\text{CO})_6$  part in Figure 3.

### Figure 2 and 3 here

Attempts to crystallize  $\text{FvW}_2(\mu\text{-S}_2)(\text{CO})_6$  by layering a sample of the reaction mixture obtained in reaction 7 with heptane over a period of 2 weeks, led to the isolation of well formed orange crystals of  $\text{FvW}_2(\mu\text{-S})(\text{CO})_6$ . The structure of this complex is shown in Figure 4. It is likely that this compound is the result of sulfur atom transfer from  $\text{FvW}_2(\mu\text{-S}_2)(\text{CO})_6$  to  $\text{HCr}(\text{CO})_3\text{C}_5\text{Me}_5$ . Indeed, a calorimetric study of reaction 7 indicated the occurrence of slow reduction of  $\text{FvW}_2(\mu\text{-S}_2)(\text{CO})_6$  to  $\text{FvW}_2(\mu\text{-S})(\text{CO})_6$  when excess  $\bullet\text{Cr}(\text{CO})_3\text{C}_5\text{Me}_5$  was present. It

was only through isolation of crystals of  $\text{FvW}_2(\mu\text{-S})(\text{CO})_6$  that identification of this product was accomplished, and the details of the reduction of  $\text{FvW}_2(\mu\text{-S}_2)(\text{CO})_6$  by  $\text{HCr}(\text{CO})_3\text{C}_5\text{Me}_5$  are not known.

**Figure 4 here**

**Structural Comparison of  $\text{FvW}_2(\text{SH})_2(\text{CO})_6$ ,  $\text{FvW}_2(\mu\text{-S}_2)(\text{CO})_6$ , and  $\text{FvW}_2(\mu\text{-S})(\text{CO})_6$ .** The full crystallographic data for the structures of  $\text{FvW}_2(\text{SH})_2(\text{CO})_6$ ,  $\text{FvW}_2(\mu\text{-S}_2)(\text{CO})_6$ , and  $\text{FvW}_2(\mu\text{-S})(\text{CO})_6$  are attached as Supplementary Information. The picture of  $\text{FvW}_2(\text{SH})_2(\text{CO})_6$  in Figure 1 is that expected for a trans-fulvalene system devoid of metal-metal or bridging ligand bonds. The two SH groups are distant in this conformation. However, it is clear that rotation around the C1-C1A bond of the bridging fulvalene ligand allows for intramolecular contact and hence reactivity. This structure was also ascertained in the cocrystallisate of  $\text{FvW}_2(\mu\text{-S}_2)(\text{CO})_6$  and  $\text{FvW}_2(\text{SH})_2(\text{CO})_6$  from reaction 6. As shown in Table 1, the data for the two determinations are in reasonable agreement and similar to those of the related complex  $\text{C}_5\text{Me}_5\text{W}(\text{CO})_3\text{SH}$ .<sup>8</sup> It is apparent that the microenvironment around the metals is essentially the same for the three compounds.

**Table 1.** Comparison of Bond Lengths and Angles of  $\text{C}_5\text{Me}_5\text{W}(\text{CO})_3\text{SH}$ ,<sup>a</sup>  $\text{FvW}_2(\text{SH})_2(\text{CO})_6$ , and  $\text{FvW}_2(\text{SH})_2(\text{CO})_6$  Cocrystallized with  $\text{FvW}_2(\text{S}_2)(\text{CO})_6$

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C <sub>5</sub> Me <sub>5</sub> W(CO) <sub>3</sub> SH		FvW <sub>2</sub> (S <sub>2</sub> )(CO) <sub>6</sub>		FvW <sub>2</sub> (SH) <sub>2</sub> (CO) <sub>6</sub> / 2 FvW <sub>2</sub> (S <sub>2</sub> )(CO) <sub>6</sub>	
W-S	2.52	W-S	2.51	W-S	2.50
W-CO <sub>avg</sub>	2.00	W-CO <sub>avg</sub>	2.00	W-CO <sub>avg</sub>	1.98
C2-W-S	75.8	C2-W-S	75.5	S1-W-C16	75.3
C1-W-S	134.5	C1-W-S	134.6	S1-W-C17	131.9
C3-W-S	78.7	C3-W-S	76.7	S1-W-C18	78.0

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<sup>a</sup> Reference 8.

The scaffold of FvW<sub>2</sub>(μ-S)(CO)<sub>6</sub> (Figure 4) can be compared to that of the analogous CpW dimer, previously reported by Kubas and coworkers<sup>6</sup> from reaction 8. In this molecule,



the two Cp groups are transoid, and the W-S-W angle is 127°, with an average W-S bond length of 2.53 Å. In FvW<sub>2</sub>(μ-S)(CO)<sub>6</sub>, in which the Cps are constrained to be cis, the W-S bonds are surprisingly unaffected (average length 2.54 Å). The W-S-W angle, however, is compressed by nearly 20° to 109.72°. This number might point to the presence of strain, to be confirmed by further thermochemical studies. On a speculative note, it has been reported that the complex C<sub>5</sub>Me<sub>5</sub>(CO)<sub>2</sub>Cr≡S≡Cr(CO)<sub>2</sub>C<sub>5</sub>Me<sub>5</sub> which contains a linear Cr≡S≡Cr framework is remarkably inert to carbonylation (and other ligand additions)<sup>1</sup> to yield (presumably angular) C<sub>5</sub>Me<sub>5</sub>(CO)<sub>3</sub>Cr-S-Cr(CO)<sub>3</sub>C<sub>5</sub>Me<sub>5</sub>. Conversely, there is no literature describing the generation of W≡S≡W complexes by decarbonylation of [CpW(CO)<sub>3</sub>]<sub>2</sub>(μ-S).



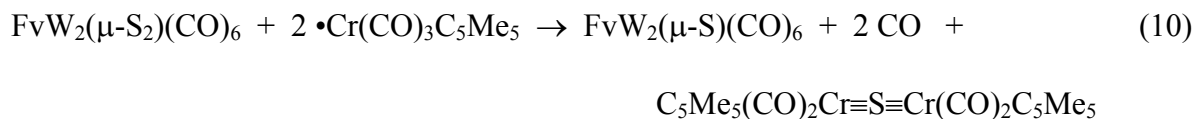
Thus, it may be that the position of equilibrium shown in eq 9 is shifted to the right for  $\text{M} = \text{Cr}$  and to the left for  $\text{M} = \text{W}$ . The effect of the fulvalene bridge on this equilibrium, as well as related structural and thermochemical questions in these sulfide complexes, are under active investigation.

Similarly, the steric strain of accommodating the  $(\mu\text{-S}_2)$ - (Figure 3) versus  $(\mu\text{-S})$ -moieties (Figure 4) warrants quantification. The W-W bond distance of 4.99 Å in  $\text{FvW}_2(\mu\text{-S}_2)(\text{CO})_6$  is much larger than that in  $\text{FvW}_2(\text{CO})_6$  of 3.347 Å and excludes any W-W bonding interaction. This distance is reduced to 4.14 Å in  $\text{FvW}_2(\mu\text{-S})(\text{CO})_6$ . The structural parameters of the coordinated disulfide appear to be in the rather wide range reported for other bridging disulfide complexes.<sup>16</sup> The two component Cp rings deviate significantly from coplanarity, a further indication of potential strain.

**Enthalpy of Sulfur Atom Insertion into  $\text{FvW}_2(\text{H})_2(\text{CO})_6$ .** The enthalpy of eq 3 was measured by solution calorimetry, and the value of  $\Delta H = -19.2 \pm 1.8$  kcal/mol in THF solution is slightly less negative than that measured for sulfurization of two molecules of  $\text{C}_5\text{H}_5\text{W}(\text{CO})_3\text{H}$ ,  $\Delta H = -22.4 \pm 0.6$  kcal/mol.<sup>8</sup> The difference (1.6 kcal/mol per reacting W-H unit) is near the limits of experimental error, indicating that the W centers in the fulvalene system operate essentially independently and that there is no significant strain associated with their conversion to dithiol.

**Enthalpy of Hydrogenation of  $\text{FvW}_2(\mu\text{-S}_2)(\text{CO})_6$ .** The enthalpy of reaction 7 was measured by solution calorimetry in toluene and found to have a value of  $\Delta H = -8.2 \pm 0.6$

kcal/mol. As reported in the experimental section, a slow side reaction occurred to a varying extent, shown in eq 10. It was judged to insignificantly influence the measured enthalpy of



reaction, as it manifested itself by only slightly endothermic tailing towards the end of the runs. Nevertheless, its presence warrants an increase in the estimated experimental error by 1 kcal/mol, suggesting a final  $\Delta H = -8.2 \pm 1.6$  kcal/mol.

We have previously measured<sup>17</sup> the enthalpy of hydrogenation of the chromium radical as shown in eq 11,  $\Delta H = -20.4 \pm 2.0$  kcal/mol. Subtraction of eq 7 from eq 11 yields directly the



enthalpy of reaction 12, the enthalpy of hydrogenation of the coordinated disulfide bond in  $\text{FvW}_2(\mu\text{-S}_2)(\text{CO})_6$ ,  $\Delta H = [-20.4 \pm 2.0 \text{ kcal/mol} - (-8.2 \pm 1.6 \text{ kcal/mol})] = -12.2 \pm 3.6$  kcal/mol. While an unfavorable entropy of reaction on the order of  $\Delta S = -25$  cal/mol deg can be



estimated,<sup>18</sup> it would not be expected to overcome the favorable enthalpy, implying that eq 12 should proceed, of interest in light of the fact that the molybdenum complex shown in eq 4



readily adds H<sub>2</sub> at atmospheric pressure. However, attempts to reduce this notion to practice were unsuccessful, even at H<sub>2</sub> pressures up to 68 atm for several days.

## Conclusions

This paper reports the first structural characterization of fulvalene derivatives of W that incorporate sulfur into the coordination chemistry of the metal: FvW<sub>2</sub>(SH)<sub>2</sub>(CO)<sub>6</sub>, FvW<sub>2</sub>(μ-S<sub>2</sub>)(CO)<sub>6</sub>, and FvW<sub>2</sub>(μ-S)(CO)<sub>6</sub>. The results, while constituting a modest foray, point to a complex, but rich chemistry that lies in store in our efforts to extend them.

Although it would be premature to generalize, it appears that the qualitative and quantitative changes often effected by linking the two Cp rings in (CpM)<sub>2</sub> complexes to give the FvM<sub>2</sub> frame will also be noticeable in the structure and chemistry of their respective sulfur derivatives. Such will be the essence of future investigations.

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**Supporting Information Available:** Complete information on data collection, atomic coordinates, thermal parameters, and structural tables for FvW<sub>2</sub>(SH)<sub>2</sub>(CO)<sub>6</sub>, FvW<sub>2</sub>(μ-S<sub>2</sub>)(CO)<sub>6</sub>, and FvW<sub>2</sub>(μ-S)(CO)<sub>6</sub>.

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